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X-ray photoemission studies of surface pre-treated graphite electrodes

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Abstract

Surface pre-treatment of graphitic electrode materials for lithium ion cells has recently been shown to significantly reduce the irreversible consumption of material and charge due to the formation of the so-called solid electrolyte interphase, during battery charging. In this paper we compare graphite powders and carbon fibres as model materials for studies of the effects of CO₂ pre-treatments on solid electrolyte interphase (SEI) formation using X-ray photoemission spectroscopy (XPS). We observe significant modification in the surface elemental composition as a function of CO₂ treatment temperature for carbon fibres, but no strong changes for graphite powders. We conclude that the predominance of the relatively unreactive basal plane in the surface area of the powders makes them far less suitable for detailed XPS studies than the fibres, where the more reactive prismatic planes predominate. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since lithium ion cells typically operate at voltages beyond the thermodynamic stability range of the organic electrolytes, electrolyte decomposition occurs. However, the resulting reaction products can form films at the electrodes which, in an ideal case, produce an electronically insulating layer, stopping further decomposition, while still permitting the transport of lithium ions. At the anode, such a film is referred to as a solid electrolyte interphase (SEI) [1,2]. SEI formation inevitably results in the partial consumption of both electrolyte and lithium, leading to a loss in charge known as the irreversible capacity, C_{irr} . This reduces the specific energy of the cell, and increases the required material expenses for cell construction, and it is, therefore, advantageous to be able to reduce C_{irr} while still forming an effective SEI.

The performance of lithium ion cells depends strongly on the type of electrode materials used, with graphitic carbons emerging as the material of choice for the anode through a combination of electrochemical, economic and environmental

reasons [1]. Graphite possesses two kinds of surfaces: the basal plane, and the prismatic (edge) surfaces. The basal plane of graphite consists largely of carbon atoms. In contrast, the considerably more heterogeneous prismatic planes include various, mostly oxygen- and hydrogen-containing, surface groups. The surface chemistry and morphology of the prismatic surfaces of graphite play a major role in chemical and electrochemical reactivity, interaction with SEI products, etc. [1–4]. Moreover, the transport of lithium ions during battery cycling largely takes place via the prismatic planes rather than the basal planes. Thus, the amount, morphology and chemical composition of the prismatic surfaces have a significant impact on the anode performance.

One route to the reduction of C_{irr} is to chemically treat the surface of the graphite prior to electrode construction. For example, we have recently shown that pre-treatment of graphite electrode materials with gaseous CO₂ at elevated temperatures produces a substantial reduction in C_{irr} [3,4]. Whereas ideal basal planes are rather unreactive, the surface chemistry of the prismatic planes may be changed significantly during the gaseous treatment at elevated temperatures, and anode performance in turn may be changed as well [3,4]. Therefore, the chemical state of the exposed prismatic planes is of considerable interest. In principle measurements by X-ray photoemission spectroscopy (XPS), which have a probing depth of ~1.5 nm for carbon [5], can be used to provide direct information on the surface chemical state of

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the exposed prismatic planes, but care has to be taken in the choice of graphitic material to be studied. The material chosen must permit XPS analysis of at least a significant proportion of prismatic surface area, and it must also be suitable for the construction of (at minimum, prototype) battery electrodes with which C_{irr} can be determined. Two graphitic materials, both of which are particularly suited to electrochemical investigations, and the construction of prototype electrodes, are graphite powders and carbon fibres. Graphite powders, with particle sizes around the 10 µm range, were used in the CO₂ studies reported earlier [3]. While there is an extensive literature on the surface properties of carbon fibres [6], XPS studies on graphitic powders are much less common.

In this paper, we compare the suitability of graphite powders and carbon fibres for XPS studies of the CO₂ treatment of graphite electrodes. SEM data [7] show that the SFG 44 powders consist of graphite platelets, where most of the surface area is the graphite basal plane, while the P100S fibres consist of a radial array of graphitic planes such that most of the surface area is prismatic planes.

The oxidation of graphite by CO₂ is endothermic, with the so-called Boudouard equilibrium (Eq. (1)) moving to the product side, i.e. CO, with increasing temperature.



At temperatures of 500°C and below combustion largely does not occur, while at 1000°C the CO₂ is able to slowly combust the graphite. Graphite powder and carbon fibre samples were prepared as a function of CO₂ treatment temperature, and their resulting surface elemental compositions compared by XPS.

2. Experimental

The XPS measurements were performed with a PHI 5400 electron spectrometer, using unmonochromated Mg K α radiation ($h\nu = 1253.6$ eV), giving an overall energy resolution of ~1 eV for survey scans. The carbon fibre samples were clamped to a gold-plated sample holder, while the graphite powder samples were mounted using double-sided conducting adhesive tape.

The graphite powders used were Timrex® special graphites SFG 44, as used in the C_{irr} studies [3,4]. The carbon fibres used were Thorne® P100S pitch based carbon fibres (Amoco). Commercially available carbon fibres for application in carbon fibre/polymer composites, such as the P100S fibres, are industrially surface treated in order to provide good adhesion of the fibre with the polymer. The detailed methods of surface treatment are proprietary and not disclosed in the literature. However, basically the industrial surface treatment involves an oxidation step and a subsequent polymer treatment step [8]. To remove the polymer from the surface, the P100S fibres were first extracted in acetone in a Soxhlet apparatus for 48 h, then dried in low

vacuum at 150°C for 4 h, and finally heat-treated in argon as described below.

The CO₂ treated samples were prepared in a two step procedure as follows. The carbon was placed in quartz glass tube and heated in a tube furnace under an argon atmosphere from room temperature to 1000°C in 20°C/min steps. The sample was held at 1000°C for 1 h in order to remove the pristine surface-groups and impurities from the carbon surface. After this “cleaning” step the carbon was either left at 1000°C, or cooled to 500 or 700°C, and treated with CO₂ for 15 min or simply cooled down to ambient temperature without further CO₂ treatment (“Ar-cleaned” carbon). After treatment the tube was cooled to room temperature under argon atmosphere, and the samples stored under dry conditions.

3. Results and discussion

Typical wide scan XPS spectra are shown in Fig. 1. Visible are the carbon and oxygen 1s photoemission peaks, and also their KLL Auger peaks, with the “stepped” background of secondary electrons characteristic of XPS. After subtraction of this background, the relative areas of the C and O photoemission peaks, taking their photoionization cross-sections into account, gives the surface elemental composition. These results are summarised in Table 1.

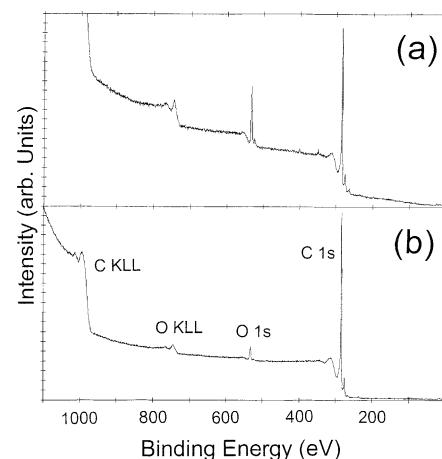


Fig. 1. Wide scan XPS spectra, normalised to the carbon 1s peak, of P100S fibres, (a) “Ar-cleaned” and (b) after CO₂ treatment at 1000°C.

Table 1
Surface elemental composition of “Ar-cleaned” and different CO₂ treated P100S fibres and SFG 44 graphite powder, as determined from XPS

	P100S		SFG 44	
	C%	O%	C%	O%
Ar, 1000°C	86.6	13.4	99.01	0.99
CO ₂ , 500°C	94.7	5.3	97.2	2.8
CO ₂ , 700°C	93.6	6.3	98.1	1.9
CO ₂ , 1000°C	91.7	8.3	96.2	3.8

The carbon percentage on all the SFG 44 surfaces is essentially constant at $97.5 \pm 1.5\%$. For the P100S fibres there is a significant difference between the surface carbon content of the Ar-cleaned sample compared to the treated material, indicating the removal of oxygen from the surface. In addition there is a small but finite decrease in the C percentage on the carbon fibres between 500 and 1000°C. Increasing the temperature for CO₂ treatment apparently results in carbon combustion and introduction of oxygen on the surface as suggested by the Boudouard equation.

4. Conclusions

The P100S data of Table 1 show CO₂ treatment temperature dependent effects, while the SFG 44 powder data are essentially constant. Several main conclusions can be drawn from these data: the chance to find oxygen in the XPS is related to the extent of prismatic surface area of a given graphite material. For the graphite powders, the proportion of prismatic to basal planes surfaces visible to XPS is simply too low for any effects to be determined unambiguously. The effect of mild surface chemical modifications as induced by CO₂ treatment is dependent on the prismatic surface area again, as the basal plane area is attacked at very strong treatment conditions only. For these two reasons, surface treatment is visible in the P100S data, but apparently absent in the SFG 44 data. We conclude that the SFG 44 powders are not particularly suited to XPS studies relevant to SEI formation, although they are the material used in actual graphite electrodes. However, the fibres provide a good model, due to the much larger proportion of prismatic surfaces visible to XPS. In addition, the fibres can also be used for electrochemical studies of SEI formation, and a

reduction in C_{irr} has in fact been observed [9] after the same CO₂ treatments which reduced C_{irr} for powder electrodes [3,4].

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